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SUPPLEMENTARY INFORMATION
SOLUBILITY AND NUCLEATION OF METHYL STEARATE AS A FUNCTION OF CRYSTALLISATION ENVIRONMENT

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ABSTRACT

Additional and more detailed materials are provided as a supplement to the paper with the above title. It includes:

1. Comparative schemes for the isothermal or the polythermal method based on a concentration vs temperature profile
2. The full derivation of the set of expressions that comprise the KBHR approach [1, 2]
3. Kerosene n-alkanes chain length distribution
4. Temperature calibration lines for the Crystal 16 unit
5. Flow chart describing how to apply the KBHR approach for the analysis of nucleation kinetics from polythermal experimental data
6. Experimental crystallisation $T_c$ and dissolution $T_{diss}$ temperatures as a function of cooling rate $q$
7. Comparative figures of nucleation kinetics parameters for methyl stearate crystallising from dodecane, kerosene and toluene solvents at the experimental crystallisation temperatures

The reference numbering in the supplementary information coincides with that in the paper. The reference to equations numbering from section 3 to 7 coincides with that in the paper.
1. Comparative schemes for the isothermal or the polythermal method based on a concentration vs temperature profile

![Diagram](image)

Fig. S1 Comparative scheme of the different approaches used to collect experimental data to assess nucleation kinetics based on a concentration vs temperature plot a) isothermal b) polythermal

2. Detailed derivation of the model equations, used to assess solution’s crystallisation kinetics, from the Kolmogorov-Johnson-Mehl-Avrami (KJMA) expression

A detailed derivation of the set of expressions that conforms the KBHR approach is presented below. Expressions for the dependence of critical undercooling on cooling rate are derived for the cases of progressive PN and instantaneous nucleation IN mechanism from the Kolmogorov-Johnson-Mehl-Avrami KJMA.

The KBHR approach makes use of a master equation presented by Kashchiev [37] that describes the first-order transition nucleation process restricted to one component nucleation by either homogeneous or heterogeneous nucleation.
In crystallisation of a single component the phase transformation kinetics can be explained by the Kolmogorov-Johnson-Mehl-Avrami *KJMA* equation [37]. The central idea of this equation is to focus on the increment in the fraction transformed and to relate it to the current value of the fraction transformed. A conversion fraction of the crystallites’ volume $\alpha$ is typically defined as

$$\alpha = \frac{V_c}{V}$$

where $V_c$ is the volume of crystallites and $V$ the total volume of solution.

Estimating the dependence of the volume of crystallites on time $V_c(t)$ from the master equation is a complex mathematical challenge especially at the late stages of crystallisation when multiple contacts between crystallites should be considered. To overcome this difficulty the *KJMA* theory assumes that $V_c$ results from nucleation of material points at a rate $J(t)$ which then only expand irreversibly in radial direction with growth rate $G(t)$ [37]. Under this assumption $V_c$ can be easily found at the early stage of crystallisation not long after the initial moment $t = 0$ when there is already a certain level of supersaturation, the whole volume of the solution is available for nucleation and there is no contact between the growing crystallites.

The obtained *KJMA* formula limited to the early stage of nucleation shows that the progression of the fraction of crystallised volume is controlled by two basic parameters of the process of crystallisation: crystallite nucleation and growth rates [1, 2, 37]

### 2.1 Progressive nucleation case
In the case of progressive nucleation the $KJMA$ formula can be expressed as [2, 37]

$$
\alpha(t) = k_v \int_0^t f(t') \left[ \int_0^{t-t'} G(t'') dt'' \right]^d dt' \quad \text{for } \alpha < 0.1
$$

(2)

where $t$ and $t'$ are time integration variables, $f$ is the time dependent rate of either homogeneous or heterogeneous nucleation, $G$ is the time dependent radial crystallites’ growth rate, $d = 1, 2, 3$ is the dimensionality of crystallites’ growth i.e. 3 for spheres or cubes, 2 for disk or plates and 1 for needle shaped crystals, $k_v (m^{3-d})$ crystallites’ growth shape factor i.e. $\frac{4\pi}{3}$ for spheres, 8 for cubes, $\pi H_0$ for disks, $4H_0$ for square plates ($H_0$ is the fixed disk or plate thickness), and $2A_0$ for needles ($A_0$ is the fixed needle cross-sectional area).

Starting at $t = 0$ from the equilibrium temperature $T_e$ at steady cooling, relative undercooling is defined as

$$
\eta = \frac{\Delta T}{T_e} = \frac{T_e - T}{T_e}
$$

(3)

where $T$ is the solution’s temperature.

From classical 3$D$ nucleation theory the rate of crystallites nucleation can be expressed in terms of relative undercooling as

$$
J(t) = K_f e^{\frac{-b}{(1-\eta)u^2}}
$$

(4)
where \( K_f \) is the nucleation rate constant and the dimensionless thermodynamic parameter \( b \) is given by

\[
b = \frac{k_n v_o^2 \gamma_{\text{eff}}^3}{k T_e \lambda^2}
\]

where \( k_n \) is the nuclei numerical shape factor i.e. \( 16\pi/3 \) for spherical nuclei and 32 for cubic nuclei, \( v_o \) is the volume occupied by a solute molecule in the crystal, \( \gamma_{\text{eff}} \) is the effective interfacial tension of the crystal nucleus, \( \lambda \) is the molecular latent heat of crystallisation and \( k \) is the Boltzmann constant.

In the same way the radial crystallite growth rate \( G(t) \) in terms of undercooling can be expressed as

\[
G(t) = m \left( \frac{T_e}{T} \right)^{m-1} K_C^m \left[ 1 - e^{\frac{-au}{(1-u)}} \right]^{nm} u^{m-1}
\]

where \( K_C \) is the crystal growth rate constant and \( n \) and \( m > 0 \) crystallites’ growth exponents. \( n = 1 \) for growth mediated by diffusion of solute and \( n = 2 \) growth controlled by the presence of screw dislocations in the crystallite. \( m \) ranges between \( \frac{1}{2} \) and 1. \( m = 1/2 \) for growth controlled by undisturbed diffusion of solute and \( m = 1 \) for growth by diffusion of solute through a stagnant layer around the crystal and normal or spiral growth limited by transfer of solute across the crystal/solution interface. At \( m = 1 \) the crystallite radius increases linearly with time \([2, 37]\) and the dimensionless latent heat of crystallisation.
\[ a = \frac{\lambda}{kT_e} \]  

(7)

Inserting equation (4) and (6) in equation (2) and defining \( t' = \left( \frac{T_e}{q} \right) x \) and \( t'' = \left( \frac{T_e}{q} \right) z \), \( \alpha \) can be expressed in terms of undercooling

\[
\alpha(u) = C_{m,d} \int_0^u e^{-\frac{b}{(1-x)x^2}} \left( \int_0^{u-x} z^{m-1} \left[ 1 - e^{-az} \right]^m dz \right) dx
\]

(8)

where the dimensionless parameter \( C_{m,d} \) is given by

\[
C_{m,d} = k \nu m^d K_f K_{\nu}^m \left( \frac{T_e}{q} \right)^{md+1}
\]

(9)

Equation (8) can be solved if the analysis is restricted to small enough values of \( u \) satisfying inequalities

\[
u < 0.1, au < 1
\]

(10)

then

\[
1 - u \approx 1 \text{ and } 1 - e^{\left( \frac{au}{1-u} \right)} \approx au
\]

(11)

With these simplifications equation (8) then becomes
\[ \alpha(u) = C_{m,d} a^{nmd} \int_0^u \frac{e^{-b x}}{x^{(n+1)m-1}} dx \]  

(12)

Likewise, it has been shown [1, 2] that the inner integral in equation (12) can be solved for small values of \( u \), satisfying

\[ u < \left( \frac{2b}{3} \right)^{1/2} \]

(13)

leading to

\[ \alpha(u) = K_{m,d} \left( \frac{u^3}{2b} \right)^{(n+1)md+1} e^{-b \frac{u}{u^2}} \]

(14)

Additionally, it was observed [2] that the exponential term in the above equation is an approximate of \( e^{(1-u)u^2} \) and thus equation (14) becomes

\[ \alpha(u) = K_{m,d} \left( \frac{u^3}{2b} \right)^{(n+1)md+1} e^{-(1-u)u^2} \]

(15)

where the dimensionless parameter \( K_{m,d} \) is given by

\[ K_{m,d} = \frac{\Gamma[(n+1)md + 1]}{(n+1)^d} k_e a^{nmd} k_f K_{G}^{md} \left( \frac{T_e}{q} \right)^{md+1} \]

(16)

and \( \Gamma \) is the gamma function.
Equation (15) can be expressed in terms of the number of crystallites upon replacing $\alpha$ by $N$ and setting $d = 0$

$$N(u) = K_N \left( \frac{u^3}{2b} \right) e^{\left[ -\frac{b}{(1-u)u^2} \right]}$$

(17)

where $K_N$ is obtained by making $K_N = K_{m,0}$ and is given by

$$K_N = \frac{VK_jT_e}{q}$$

(18)

If plots of $\alpha$ and $N$ are constructed as a function of $u$, they show that $\alpha$ and $N$ are monotonically increasing functions of $u$, with a sharp rise at a certain value that corresponds to the relative critical undercooling for crystallisation $u_c$ [2] defined as

$$u_c = \frac{\Delta T_c}{T_e}$$

(19)

where

$$\Delta T_c = T_e - T_c$$

(20)

Here $T_c$ is the crystallisation temperature

For $u < u_c$ crystallites are so small or few that $\alpha$ and $N$ cannot be detected or are below the detection limit $\alpha_{det}, N_{det}$. For $u > u_c$ the solution will contain big enough crystallites that $\alpha$
and \( N \) will be detected \( \alpha > \alpha_{\text{det}} \) and \( N > N_{\text{det}} \). This means \( u_c \) is the maximum relative undercooling that a solution can sustain without detectable crystallisation. In other words, \( u_c \) represents the solution metastability limit in terms of undercooling \([1,2]\). This limit, however, depends on a number of parameters among which one of the most featured is the cooling rate \( q \). With the help of the previously presented equations for \( \alpha \) and \( N \), the \( u_c(q) \) dependence can be determined.

Expressing equation (17) it in terms of \( u_c \) gives

\[
N(u_c) = N_{\text{det}} = \frac{VK_fT_e}{q} \left( \frac{u_c^3}{2b} \right) e^{\left[ -\frac{b}{(1-u_c)u_c^2} \right]} \tag{21}
\]

Upon taking logarithms at both sides of equation (21) a model expression that relates relative critical undercooling \( u_c \) with cooling rate \( q \) is obtained

\[
\ln q = \ln \left( \frac{VK_fT_e}{N_{\text{det}} 2b} \right) + 3 \ln u_c - \frac{b}{(1-u_c)u_c^2} \tag{22}
\]

Likewise, if the parameters \( q_0 \), \( a_1 \) and \( a_2 \) are defined by

\[
a_1 = 3 \tag{23}
\]

\[
a_2 = b \tag{24}
\]

\[
q_0 = \frac{VK_fT_e}{N_{\text{det}} 2b} \tag{25}
\]
Then the latter equation becomes

\[ \ln q = \ln q_0 + a_1 \ln u_c - \frac{a_2}{(1 - u_c)u_c^2} \] (26)

When equation (26) is derived by means of \( \alpha \), the parameters \( q_0 \), \( a_1 \) and \( a_2 \) are defined by

\[ a_1 = 3 + \frac{3nmd}{md + 1} \] (27)

\[ a_2 = \frac{b}{md + 1} \] (28)

\[ q_0 = T_e \left\{ \frac{\Gamma[(n + 1)md + 1]}{(n + 1)^d(2b)^{(n+1)md+1}} \frac{1}{\alpha_{det}} \right\}^{(md+1)} \] (29)

The parameters in equation (26) \( \ln q_0 \), \( a_1 \) and \( a_2 \) have a physical meaning. \( a_1 \) has a relation with the crystallites growth as its values are determined by the growth exponents \( n, m \) and \( d \). \( a_2 \) is proportional or equal to the thermodynamic nucleation parameter \( b \) and \( q_0 \) has a relation with parameters of both nucleation and crystallite growth processes.

### 2.2 Instantaneous nucleation case

In the case of instantaneous nucleation \( IN \) a similar derivation was done [1] but taking into account that for the case of \( IN \) all crystallites nuclei appear at once with a concentration \( C_o \) at
the moment \( t_0 \). Thus the change of the volume of crystallites with time will only depend on the crystallites’ growth and can be expressed as

\[
\alpha(t) = k_v C_o \left[ \int_{t_0}^{t} G(t') \, dt' \right]^d
\]  

(30)

Where \( t' \) time integration variables, \( d = 1, 2, 3 \) dimensionality of crystallite’s growth, \( k_v \, (m^{3-d}) \) crystallite’s growth shape factor.

Using equation (6) and setting \( t' = \frac{t}{q} \) an expression for \( \alpha \) in terms of \( u \) can be found

\[
\alpha(u) = C_{m,d} \left( \int_{u}^{1} x^{m-1} \left[ 1 - e^{-ax} \right]^n \, dx \right)^d
\]  

(31)

where the dimensionless parameter \( C_{m,d} \) is given by

\[
C_{m,d} = k_v m^d C_o \left( \frac{K_0 T_e}{q} \right)^{md}
\]  

(32)

For small enough undercooling

\[
u < 0.1, au < 1
\]  

(33)

in which case
\[1 - u \approx 1 \quad \text{and} \quad 1 - e^{\frac{-au}{1-u}} \approx au\] (34)

The integral in equation (31) can be solved leading to

\[\alpha (u) = K_{m,d} \left[ u^{(n+1)m} - u_o^{(n+1)m} \right] \] (35)

In this expression \(u_o\) is the relative undercooling at the time \(t_o\) and is given by

\[u_o = \frac{\Delta T_o}{T_e} = \frac{q t_o}{T_e} \] (36)

Here \(\Delta T_o\) is defined by

\[\Delta T_0 = T_e - T_0\] (37)

where \(T_o\) is the solution temperature at the time \(t_o\)

Likewise, \(K_{m,d}\) is given by

\[K_{m,d} = \frac{k_v C_o \left( \frac{a^n K G T_e}{q} \right)^{md}}{(n+1)^d} \] (38)

As in the case of progressive nucleation \(\alpha\) is a monotonically increasing function of \(u\) [1] with a sharp rise at a certain value that corresponds to the relative critical undercooling \(u_c\).
Therefore defining $\alpha(u_c) = \alpha_{det}$ and taking logarithms at both sides of equation (35), an expression can be obtained for the dependence of relative critical undercooling on cooling rate

$$\ln q = \ln q_0 + \left(\frac{1}{m}\right) \ln \left[u_c^{(n+1)m} - u_0^{(n+1)m}\right]$$  \hspace{1cm} (39)

In this expression $u_0 \geq 0$, $u_c > u_0$ and the parameter $q_0$ is given by

$$q_0 = \left[\frac{k_f C_o}{(n + 1)^d \alpha_{det}}\right]^{\frac{1}{md}} a^n K_0 T_e$$  \hspace{1cm} (40)

If additionally, the undercooling at which all nuclei spontaneously appear is small enough so that

$$u_o^{(n+1)m} \ll u_c^{(n+1)m}$$  \hspace{1cm} (41)

Equation (39) takes the form of a straight line given by

$$\ln q = \ln q_0 + (n + 1) \ln u_c$$  \hspace{1cm} (42)

It should be noted that a comparison of equation (39), with the one obtained for $PN$ derived by means of $\alpha$, which is defined as

$$\ln q = \ln q_0 + \left(3 + \frac{3nm^d}{md + 1}\right) \ln u_c - \frac{a_2}{(1 - u_c)u_c^2}$$  \hspace{1cm} (43)
shows how the dependence of the relative critical undercooling $u_c$ on the cooling rate $q$ is different depending of the mechanism by which nucleation takes place. In the case of $PN$ the expression contains parameters depending on both crystallites nucleation and growth whereas in the case of $IN$ the parameters in the expression are only related to the crystallite’s growth.

2.3 The nucleation rate $J$

The nucleation rate $J$ given by expression (4) equates that given by 3D classical nucleation theory expressed in terms of relative critical undercooling $u$.

The classical theory equation for nucleation is given by expression (44)

$$J = K_f \exp \left[ \frac{k_n v_0^{2} \gamma_{e}^{3}}{(kT)^{3} (ln S)^{2}} \right]$$  \hspace{1cm} (44)

Due to the drop of $T$ during cooling, $J$ changes primarily because of the strong temperature dependence of the exponential factor. In this factor, $C_e$ is an exponential function of $T$ which can be approximated by the integrated van’t Hoff equation

$$C_e(T) = C_r e^{\frac{-\lambda}{RT}}.$$  \hspace{1cm} (45)

Here the reference solute concentration $C_r$ and the molecular latent heat of crystallisation $\lambda$ are weak functions of temperature and can be treated as $T$-independent. Since $T$ and $C$ equal their equilibrium values $T_e$ and $C_e$ when cooling commences according to equation (45) we have
\[ C = C_r \exp \left( -\frac{\lambda}{k T_e} \right) \]  

(46)

and hence

\[ \frac{C}{C_e} = \exp \left( \frac{\Delta T}{\kappa T_e} \right) \]  

(47)

where \( \Delta T = T_e - T \) is the undercooling.

Thus combining equation (44) and (47) yields

\[ J = K_f \exp \left[ -\frac{b}{\left( 1 - \frac{\Delta T}{T_e} \right) \left( \frac{\Delta T}{T_e} \right)^2} \right] \]  

(48)

where the dimensionless thermodynamic parameter \( b \) is given by equation (5)
3. Kerosene n-alkanes chain length distribution

Fig. S2 Kerosene n-alkane mass fraction distribution as obtained by 2D Gas Chromatography analysis performed by Infineum UK

4. Temperature calibration lines for the Crystal 16 unit

Temperature calibration lines for dodecane, kerosene and toluene solvents are provided below. These are obtained by plotting the temperature at which the Crystal 16® is programmed against the actual temperature of the solvent as measured by a calibrated thermocouple.
Fig. S3 Temperature calibration for the Crystal 16 unit for a) dodecane, b) kerosene and c) toluene solvents.

a) \[ y = 0.8684x + 2.1967 \quad R^2 = 0.9998 \]
b) \[ y = 0.9598x + 1.3396 \quad R^2 = 0.9997 \]
c) \[ y = 0.9543x + 0.9878 \quad R^2 = 0.9994 \]
5. Flow chart describing how to apply the KBHR approach for the analysis of nucleation kinetics from polythermal experimental data

1. Prepare binary mixture: solute viscosity must remain virtually unchanged in T range studied & its solubility increase with increasing temperature

2. Use polythermal method to obtain average values of Tn at different cooling rates q

3. Obtain relative critical undercooling u as a function of cooling rate q using equation (5)

4. Construct plot of ln q Vs ln u & fit experimental data points by a straight line

5. Apply the RULE OF THREE

6. Evaluate inequalities (20)

INSTANTANEOUS NUCLEATION

6. Evaluate inequalities (20)

Solve the KIMA formula numerically. See supplementary material

Linear Coefficient of determination

No

Yes

Fig. S4 Flowchart describing the procedure to follow in order to apply (KBHR) approach for the interpretation of metastable zone width data (MSZW) collected by means of the polythermal method
6. Experimental crystallisation $T_c$ and dissolution $T_{diss}$ temperatures as a function of cooling rate $q$

Table S1. Average dissolution ($T_{diss}$) and crystallisation ($T_c$) temperatures as a function of cooling rate for methyl stearate in dodecane, kerosene and toluene at solution concentrations 200, 250, 300 and 350 g/L of solvent for the first two solvents and 154, 192, 231 and 269 g/L of solvent for toluene. Standard deviation (SD) of crystallisation and dissolution temperatures. Relative critical undercooling $\mu_c$ calculated according to equation (5). Equilibrium temperatures $T_e$ obtained from extrapolation of best-fit straight lines through $T_{diss}(q)$ data points.

<table>
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<th>Rate °C/min</th>
<th>$T_c$ (°C)</th>
<th>SD $T_c$ (°C)</th>
<th>$T_{diss}$ (°C)</th>
<th>SD $T_{diss}$ (°C)</th>
<th>$\mu_c$</th>
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7. Comparative plots of nucleation kinetic parameters for methyl stearate crystallising from dodecane, kerosene and toluene solvents

Fig. S5 shows the results for each of the nucleation parameters obtained as a function of solvent and solution concentration at the corresponding experimental crystallisation temperatures i.e. the crystallisation temperatures obtained from the extrapolated lines to 0°C/min for the dependence of crystallisation temperature \( T_c \) on cooling rate \( q \), at each of the chosen solutions’ concentrations.

Given that these plots are not obtained at iso-supersaturation values they can be used to perform only an initial screening of the behaviour of methyl stearate nucleation as a function of crystallisation environment. From the engineering point of view Fig S5. shows practically the impact of solution environment on nucleation parameters at the experimental crystallisation temperatures e.g. that interfacial tensions are higher in toluene, which has a direct impact on the nucleation rates in this solvent where they are the lowest.
Fig. S5 Comparison of nucleation kinetics parameters for methyl stearate crystallising from dodecane, kerosene and toluene solvents at different solution concentrations. a) interfacial tension $\gamma$; b) critical radius $r^*$; c) number of crystals at the detection point $N_{det}$ and d) nucleation rates $J$. 

![Graphs showing comparison of nucleation kinetics parameters for methyl stearate crystallisation.](image-url)